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Comparison of Polyurethane Foam and XAD-2 Resin as Collection Media for Polynuclear Aromatic Hydrocarbons in Air

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The objective of this project was to evaluate the collection and retention efficiency for polynuclear aromatic hydrocarbon (PAH) adsorbed or spiked on polyurethane (PUF) and XAD-2 cartridges, and to compare the effect of sampling temperature on retention efficiency for PAH spiked on PUF and XAD-2 resin cartridges.

It appeared that XAD-2 resin has better collection efficiency for volatile 2-ring PAH than does the PUF. In addition, some spiked volatile and reactive PAH were well retained on XAD-2 resin, whereas only a small portion of these compounds is retained on PUF after exposure to ambient air at a 6.7 cfm flow rate for 24 hours. The retention efficiency for volatile PAH can be improved by lowering sampling temperature. However, the retention efficiency for reactive PAH such as cyclopenta[c,d]pyrene cannot be improved at lower sampling temperature. The losses of cyclopenta[c,d]pyrene are not through volatilization but are due to the reactivity of this compound.

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FOREWORD

Measurement and monitoring research efforts are designated to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The evaluation of XAD-2 resin and polyurethane foam for collection of polynuclear aromatic hydrocarbons provides important information that can be applied to the measurement of the extent of human exposure to the polynuclear aromatic compounds.

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ABSTRACT

The objective of this project was to (1) evaluate the collection and retention efficiency for polynuclear aromatic hydrocarbons (PAH) adsorbed or spiked on polyurethane (PUF) and XAD-2 cartridges, and (2) to compare the effect of sampling temperature on retention efficiency for PAH spiked on PUF and XAD-2 resin cartridges.

Six EPA medium volume samplers were set up to collect ambient air for 24 hours at a 6.7 cfm flow rate. Quartz fiber filters and XAD-2 resin or quartz fiber filters and PUF in series were used to collect particulate-bound PAH and vapor-phase PAH. Prior to sampling, two PUF and two XAD-2 cartridges were spiked with known amounts (2 µg of each compound) of native and perdeuterated PAH. One PUF and one XAD-2 resin cartridge were not spiked and were used as background samples. This experiment was performed at two different ambient temperature ranges: 66-86°F and 17-27°F. The filter samples were not analyzed in this study. The XAD-2 samples were extracted with methylene chloride, and the PUF samples were extracted with 10 percent diethyl ether in hexane. These sample extracts were then analyzed by electron impact gas chromatography/mass spectrometry.

The results from the non-spiked samples showed that the levels of PAH were in good agreement between the two adsorbents except for some volatile PAH, such as naphthalene. The levels of XAD-2-adsorbed naphthalene were more than 10 times higher than those of PUF-adsorbed naphthalene. For the spiked PAH, good recoveries were obtained from both adsorbents, except for a few compounds. The spiked XAD-2 resin gave substantially higher recoveries than did the spiked PUF, and approximately 80 percent of the spiked D_8-naphthalene was recovered from XAD-2 after ambient air exposure even at summer ambient temperatures (66-86°F). Low recoveries of D_{10}-phenanthrene were observed from PUF in the summer experiment, but these recoveries improved significantly in the winter experiment at lower sampling temperatures. Thus, the loss of this PAH was mainly due to volatilization. The recoveries of some other PAH were also improved to some extent from both adsorbents at lower sampling temperatures. A lower recovery of cyclopenta[c,d]pyrene was obtained from PUF than from XAD-2 resin. The recovery of this compound did not improve at lower sampling temperatures. In fact, its recoveries were smaller at lower temperatures for both adsorbents. It appears that cyclopenta[c,d]pyrene is lost not through volatilization, but through degradation. Thus, XAD-2 resin has higher collection efficiency for volatile PAH than PUF, as well as higher retention efficiency for both volatile and reactive PAH. The retention efficiency for some volatile PAH for both adsorbents can be improved by lowering the sampling temperature.

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LIST OF ABBREVIATIONS

amp	ampere
ANTHR	anthracene
BAA	benz[a]anthracene
BAP	benzo[a]pyrene
BEP	benzo[e]pyrene
CcdPYR	cyclopenta[c,d]pyrene
CHRY	chrysene
cfm	cubic feet per minute
DMSO	dimethyl sulfoxide
EI	electron impact
FLUOR	fluoranthene
GC/MS	gas chromatography/mass spectrometry
MID	multiple ion detection
PAH	polynuclear aromatic hydrocarbons
PHEN	phenanthrene
PUF	polyurethane foam
PYR	pyrene

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SECTION 1

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) have been extensively studied and have received increased attention in studies of air pollution in recent years because some of these compounds are highly carcinogenic or mutagenic. To understand the extent of human exposure to PAH, reliable sampling and analytical methodology must be established for monitoring the concentrations of these compounds in air. In general, the analytical methodology is well developed, but the sampling procedures can often reduce the validity of analytical results (1). Several studies have shown that the two- to four-ring PAH in air may be mainly in the vapor phase and are not retained by filters because of volatilization (2-4). Quartz fiber and glass fiber filters are typically used in sampling air particles. A wide variety of adsorbents such as Tenax GC, XAD-2 resin and polyurethane foam (PUF) has been used to sample PAH vapors. All these absorbents have been demonstrated to have a high collection efficiency for certain PAH. Each of these adsorbents has several drawbacks as well as virtues. For instance, Tenax GC is expensive and requires a lengthy purification procedure prior to use. It is also known to degrade to diphenylquinones, if exposed to hot, oxidizing conditions such as those in stack gas emissions (5). Both XAD-2 resin and PUF have been successfully used in air sampling for PAH. The overall comparative effectiveness of these adsorbents and the degree to which quantification of the PAH is affected by sampling, handling and storage, however, have not been fully investigated. Recently, Battelle has conducted studies (6,7) to evaluate the stability of PAH collected on PUF or XAD-2 resin and quartz fiber filters as a function of storage conditions. For comparison, the collection and retention efficiency of PUF and XAD-2 resin for PAH was investigated in this project.

The objective was to evaluate the collection and retention efficiency for PAH adsorbed or spiked on PUF and XAD-2 resin cartridges, and to compare the effect of sampling temperature (summer and winter ambient temperatures) on the retention efficiency of these two adsorbents for PAH.

SECTION 2

CONCLUSIONS

In general, only 2- to 4-ring PAH were collected on the backup adsorbent, and the nonvolatile PAH were collected mainly on the front filters. The level of PAH in ambient air collected on the PUF cartridge was comparable to that collected on the XAD-2 resin cartridge except for few volatile PAH. For example, the levels of naphthalene found in the XAD-2 resin cartridge were at least 10 times higher than those found in the PUF cartridge at both sampling temperature ranges. The amounts of phenanthrene collected on XAD-2 resin were slightly higher than those collected on PUF cartridge in the summer experiment, however identical amounts of this compound were collected on both adsorbents in the winter experiment. The XAD-2 resin cartridge appeared to have a higher collection efficiency for volatile PAH than did the PUF cartridge. The collection efficiency of PUF for some volatile PAH, such as phenanthrene, can be improved by sampling at lower temperatures.

Good recoveries of most of the spiked PAH from both adsorbents were obtained after exposure to ambient air at a 6.7 cfm (190 l/min) flow rate for 24 hours at summer and winter ambient temperatures. Exceptions to these good recoveries were observed for naphthalene, phenanthrene, and cyclopenta[c,d]pyrene. The D_8-naphthalene was well retained on XAD-2 resin whereas only a small portion (<5 percent of total) of this compound was retained on PUF. The D_{10}-phenanthrene recoveries from PUF were lower than those from XAD-2 resin in the summer experiment, but the recoveries of this compound from PUF improved significantly in the winter experiment. Some other PAH also showed higher retentions on both adsorbents at lower sampling temperatures. Lower recoveries of cyclopenta[c,d]pyrene were observed from PUF than from XAD-2, and these recoveries did not improve at lower sampling temperatures. Thus the losses of cyclopenta[c,d]pyrene are probably due to

chemical reactivity of the relatively localized carbon-carbon double bond in this compound, which is highly susceptible to oxidation.

In conclusion, XAD-2 resin has better collection and retention efficiency for volatile and reactive PAH than does PUF. Lower sampling temperature can improve the retention efficiencies of both adsorbents for some volatile PAH, but not for reactive PAH. Therefore, despite the fact that the PUF cartridge is easily handled in the field and has better flow characteristics, XAD-2 resin is a better choice of adsorbents in air sampling for 2-4 ring PAH.

SECTION 3

RECOMMENDATIONS

Losses of reactive PAH during sampling and sample storage have been confirmed both in this study and a previous study (7). The reactive PAH, cyclopenta[c,d]pyrene, contains a five-membered ring and is readily oxidizable due to the olefinic nature of the relatively localized carbon double bond. One research group has reported (8) that pyrene-1,10-dicarboxylic anhydride, a direct-acting mutagen, is a possible oxidative derivative of cyclopenta[c,d]pyrene. Another research group (9) found a dicarboxylic acid anhydride of a PAH with molecular weight of 202 in airborne particulate matter. The possible parent PAH compounds with molecular weights of 202, acephenanthrylene and aceanthrylene, also have five-membered rings that are readily oxidized. Since some of these oxidized PAH derivatives show mutagenicity, we recommend that a study be conducted to determine to what extent these compounds are sampling artifacts and to what extent they are actual pollutants in ambient air.

The bioassays conducted by EPA/HERL/RTP showed that the air sample extracts obtained in this study contained mutagens. Some of the mutagenic activity can be accounted for by PAH. Other classes of compounds present in the extracts, however, may be important contributors to mutagenic activity. We recommend that a study be conducted to characterize the mutagens or carcinogens in the air sample extracts. Because the determination of the specific mutagens or carcinogens is limited by the complexity of the extracts, the most cost-effective approach is the bioassay-directed fractionation and characterization method. We recommend the use of open bed silica gel column chromatography to remove the non-active aliphatic compounds. The remaining extracts would be further sub-fractionated by high-performance liquid chromatography (HPLC). Bioassays would be conducted on each of these HPLC sub-fractions. The most active fractions would be analyzed by various methods to

identify the unknown mutagens or carcinogens. If a HPLC fraction were still too complex for single component identification, it would be subjected to secondary HPLC fractionation. The analytical techniques that could be used include:

(1) HPLC/MS with moving belt and/or thermospray interface for the determination of polar compounds.

(2) Fast Atom Bombardment-Mass Spectrometry (FAB-MS) for the determination of compounds of low volatility or high molecular weight (eg. M/Z = 10,000).

(3) Comparative electron impact and negative or positive chemical ionization GC/MS for identification of unknown compounds.

(4) Tandem mass spectrometry (MS/MS) for the determination of unknown compounds. The MS/MS could be operated in constant neutral loss, parent ion or daughter ion modes. The combination of these modes will allow the determination of fragmentation patterns and also molecular structures of unknown components.

SECTION 4

EXPERIMENTAL PROCEDURES

SAMPLE COLLECTION

Six EPA medium volume samplers (modified General Metals PS-1 samplers with General Metals bypass motors in place of the original high-volume blower motors) were employed. Quartz fiber filters, followed by XAD-2 resin or PUF in series, were used to collect particulate matter and vapors. Samplers were located on the ground in an open space area outside Battelle away from any exhaust openings or heavy traffic. Two sets of three samplers were located in parallel approximately two feet apart. In each set, the samplers were placed about one foot apart. A five foot long exhaust hose leading away from the sampler inlet was attached to each sampler to avoid recirculating the exhaust air to the filter and the adsorbent. Prior to sampling, each sampler was calibrated with a Rockwell Model 415 dry gas meter. Adjustments were made with a control and a bypass valve to obtain a flow rate of 6.7 cfm (190 l/min). Two of the cleaned XAD-2 and two of the PUF cartridges were spiked with 200 µl of methylene chloride solution containing 10 µg/ml of each of the native and perdeuterated PAH. Prior to sampling, exactly 200 µl of the spiking solution was withdrawn into a 250-µl syringe, and the solution was injected approximately 1 in. deep into the clean adsorbent. One PUF and one XAD-2 cartridge were not spiked with PAH and were retained as background samples. Air was then sampled for 24 hours so that a total volume of approximately 273 m^3 was sampled. During the sampling period, the flow rate was checked approximately every 4 hours. After sampling, a final flow check was conducted on each sampler. All PUF and XAD-2 cartridges, as well as filters, were wrapped with aluminum foil and transported to the laboratory for analysis. This experiment was performed in the summer with ambient temperatures of 66-86°F, and was repeated under the same conditions in the winter with ambient temperatures of 17-27°F.

PREPARATION OF ADSORBENTS

The PUF cartridges were purchased from Southwest Research Institute. The PUF cleanup procedure consisted of sequential compression/decompression of the PUF plug in 800 ml each of toluene, acetone, and 5 percent ether/hexane. This was followed by Soxhlet extraction for 16 hours with acetone, and drying in a vacuum oven at room temperature. The clean PUF (2.2 in. I.D., 3 in. length) was placed in a clean glass cartridge (2.3 in. I.D., 5 in. length), wrapped with hexane-rinsed aluminum foil, and stored in a clean screw-capped jar. All PUF plugs were cleaned by this procedure before air sampling.

The pre-cleaned XAD-2 resin was purchased from Supelco. This pre-cleaned resin was Soxhlet-extracted with methylene chloride for 16 hours and dried with an ultra-pure nitrogen gas stream. The clean XAD-2 resin was placed in a glass cartridge of the same type that was used for the PUF plug. A nickel wire screen was fit to the bottom of the glass cartridge to retain the XAD-2 resin. The mesh size of the screen was 200/200 and the wire size was 0.0021-0.0022 in. The XAD-2 resin bed depth was 2 in., which allows a maximum sampling flow rate of approximately 7 cfm. The mass of XAD-2 used was 55 g per cartridge.

PREPARATION OF STANDARD SOLUTIONS

The spiking solution, containing selected native and perdeuterated PAH at a concentration of 10 µg/ml for each compound, was prepared in methylene chloride and was stored in a 100 ml volumetric flask. The spiked PAH compounds are listed in Table 4.1. Four 1 ml aliquots of the spiking solution were transferred into four 2-ml GC vials for field use.

Aliquots of the spiking solution were used to prepare the standard solutions for GC/MS analysis. Four concentrations, 5.0 µg/ml, 2.0 µg/ml, 0.50 µg/ml, and 0.10 µg/ml were prepared by dilution with cyclohexane. The GC/MS internal standard, 9-phenylanthracene, was added to each standard solution at a constant concentration of 1.0 µg/ml.

TABLE 4.1. PAH COMPOUNDS IN THE SPIKING SOLUTION

Compound	M/Z
D_8-naphthalene	136
D_{10}-phenanthrene	188
Phenanthrene	178
Anthracene	178
Fluoranthene	202
D_{10}-pyrene	212
Pyrene	202
Cyclopenta[c,d]pyrene	226
Benz[a]anthracene	228
D_{12}-chrysene	240
Benzo[e]pyrene	252
D_{12}-benzo[a]pyrene	264
Benzo[a]pyrene	252

PREPARATION OF SAMPLE EXTRACTS

The filter samples were stored in the dark at room temperature and were not analyzed in this study. The XAD-2 samples were Soxhlet-extracted with 800 ml of methylene chloride. Since methylene chloride is not a suitable solvent for PUF, the PUF samples were extracted with 800 ml of 10 percent ether in hexane. The extraction was carried out for at least 16 hours and until the solution in the Soxhlet extractor's top chamber became clear. After extraction, the sample extract was concentrated by Kuderna-Danish evaporation to a final volume of 1 ml. The internal standard, 9-phenyl anthracene, was added to all sample extracts at a level of 1.0 µg/ml prior to GC/MS analysis.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Electron impact gas chromatography/mass spectrometry (EI GC/MS) in the multiple ion detection (MID) mode was employed to determine the native PAH and the perdeuterated PAH. The instrumentation conditions used are summarized in Table 4.2. A Finnigan Model 4500 quadrupole mass spectrometer equipped with an EI/CI source was used for the analyses. The molecular ion of each target compound was monitored. The ion source temperature was held at 180°C, and the electron multiplier was operated at a gain of approximately 10^5.

An Ultra No. 2 fused silica capillary column (50 m x 0.31 mm I.D., 0.51 µm film thickness, Hewlett-Packard Co.) with methane carrier gas was used for analyte separation. The GC column was interfaced directly to the MS ion source. The GC column temperature was held at 45°C for 1 min, programmed rapidly to 100°C in 5 min, and then programmed from 100°C to 320°C at 8°C/min.

The standard solutions and sample extracts were analyzed by EI GC/MS. Identifications of the PAH compounds in the sample extracts were based on the correct ion mass and the correct retention time relative to the internal standard, as determined from the standard analyses. The standard analyses were also used to calculate the response factor for each compound relative to the internal standard. The following equation was used for quantification:

TABLE 4.2. GC AND MS OPERATING CONDITIONS

Chromatography	
Column	HP Ultra #2 crosslinked 5% phenyl methyl silicone 50 m x 0.31 mm, 0.51 μm film thickness
Carrier Gas	CH_4
Injection Volume	2 μl
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	45°C
Initial Hold Time	1 min
Program	45°C to 100°C in 5 min, then 100°C to 320°C at 8°C/min
Final Hold Time	15 min
Mass Spectrometer	
Ionization	Electron impact at 70 eV
Emission Current	0.3 m amp
Preamplifier	10^{-8} amp/volt
Detection Mode	Multiple ion detection

$$C_x = \frac{A_x \times C_{is} \times FV}{A_{is} \times R_f}$$

where:

C_x = Total amount of a target compound in the extract, µg

A_x = Molecular ion integration area of a target compound

C_{is} = Concentration of the internal standard, µg/ml

A_{is} = Molecular ion integration area of the internal standard

R_f = Response factor of a target compound

FV = Final volume of the extract, ml.

EXTRACT PREPARATION FOR MICROBIOASSAY

Since the microbioassay is conducted directly in the vials containing the sample extracts, the vials must be clean and free of chemical or biological interference. Therefore, prior to solvent exchange, the vials to be used for bioassay were placed in a oven and heated overnight at 500°C. The screw caps of these vials were Soxhlet-extracted with methanol for 16 hours. The extracted screw caps were dried with a nitrogen gas stream and all the clean vials were sealed with the clean screw caps prior to solvent exchange.

Sample extracts from the PUF and XAD-2 background samples and field blanks were diluted to 1.0 mg/ml with methylene chloride. Aliquots of the diluted extracts (1.0 mg/ml) to give different masses of extracted organic material as shown in Table 4.3 were placed in different sample vials. The sample extracts were then evaporated to near dryness under a gentle nitrogen stream and 2 µl of dimethyl sulfoxide (DMSO) were added to each sample vial. The DMSO samples were mixed with a Vortex mixer and evaporated under nitrogen for an additional five minutes. Then the sample vials were sealed with screw caps and immediately stored under dry ice. These samples were packed in dry ice and sent to EPA at HERL/ERC/RTP for microbioassay.

TABLE 4.3. CHARACTERISTICS OF THE SAMPLE EXTRACTS PREPARED FOR MICROBIOASSAY

Sample Code[a]	Dose Level, µg/vial	Number of Vials Prepared
XAD 1	400,200,100,50,20	4
PUF 1	400,200,100,50,20	2
XAD B1	normalized 400,200,100,50,20[b]	4
PUF B1	normalized 400,200,100,50,20	2
XAD Solvent Blank	normalized 400,200,100,50,20	2
PUF Solvent Blank	normalized 400,200,100,50,20	2
XAD 1R	400,200,100,50,20	2
PUF 1R	400,200,100,50,20	2
XAD B2	normalized 400,200,100,50,20	2
PUF B2	normalized 400,200,100,50,20	2
XAD Solvent Blank	normalized 400,200,100,50,20	1
PUF Solvent Blank	normalized 400,200,100,50,20	1

(a) XAD 1 and PUF 1 are the background samples and XAD B1 and PUF B1 are the field blanks from the summer experiment; XAD 1R and PUF 1R are the background samples and XAD B2 and PUF B2 are the field blanks from the winter experiment.

(b) The doses of the XAD-2 and PUF field blanks and solvent blanks for bioassay are not aliquotted by mass but by a volume equivalent to that used for the corresponding XAD and PUF samples which are designated as normalized mass dose levels.

SECTION 5

RESULTS AND DISCUSSION

The PUF and XAD-2 sample extracts were analyzed by EI GC/MS to determine the levels of PAH. The results are summarized in Tables 5.1 through 5.4. The levels of PAH found in the field PUF and XAD-2 resin blanks are given in Table 5.5. The PAH ambient background levels determined from both adsorbents are summarized in Figure 5.1. The average recoveries of the spiked PAH determined from both adsorbents are given in Figures 5.2 and 5.3.

As shown in Table 5.5, none of perdeuterated PAH were found in either the PUF field blanks or the XAD-2 resin field blanks. Only trace amounts of phenanthrene, anthracene, pyrene, and fluoranthene were found in the PUF and XAD-2 resin field blanks.

The XAD-2 samples were extracted with methylene chloride to remove PAH from XAD-2 resin. Since methyl chloride is not a suitable solvent for PUF, 10 percent ether in hexane was used as extraction solvent for PUF. In our previous study (10), it was demonstrated that the Soxhlet extaction method using 10 percent ether in hexane can successfully remove PAH from PUF. Even though different solvents were used for XAD-2 and PUF, that should not affect the relative amounts of PAH recovered from both adsorbents.

The sampling experiment was conducted during the summer, then repeated in the winter. In each experiment, all six runs were made simultaneously under identical sampling conditions. Therefore, the variation within each run associated with the sampling and analytical procedures is estimated to be within 20 percent based on a previous study (6). Within each experiment, the agreement between PAH ambient background levels determined from PUF and XAD-2 resin cartridges is very good except for a few volatile PAH. As shown in Figure 5.1, the naphthalene levels in the XAD-2 resin cartridges were more than 10 times higher than those in the PUF cartridges from both the summer and

TABLE 5.1. LEVELS AND RECOVERIES OF PAH IN PUF CARTRIDGES IN THE SUMMER EXPERIMENT

Compound	Total Amount, μg[a]			Percent of Recovery, %		
	PUF 1	PUF 2	PUF 3	PUF 2	PUF 3	Average
D_8-naphthalene	--[b]	--	--	0.0	0.0	0.0
D_{10}-phenanthrene	--	0.02	0.06	1.0	3.0	2.0
Phenanthrene	36.7	39.6	38.0	140[c]	65[c]	103
Anthracene	1.05	1.31	1.22	13.0	8.5	11
Fluoranthene	12.8	16.2	13.8	170[c]	50[c]	110
D_{10}-pyrene	--	1.73	1.76	87	88	88
Pyrene	3.60	5.73	5.35	110	88	99
Cyclopenta[c,d]pyrene	--	0.75	0.80	38	40	39
Benz[a]anthracene	--	1.25	1.34	63	67	65
D_{12}-chrysene	--	1.51	1.72	76	86	81
Benzo[e]pyrene	--	1.47	1.73	74	87	81
D_{12}-benzo[a]pyrene	--	1.07	1.14	54	57	56
Benzo[a]pyrene	--	1.22	1.24	61	62	62

(a) PUF 1 was the non-spiked sample; PUF 2 and PUF 3 were spiked with 2 μg of the listed PAH prior to sampling; a total of 273 m^3 of air was sampled.

(b) Not detected.

(c) The recovery cannot be accurately addressed due to high background levels.

TABLE 5.2. LEVELS AND RECOVERIES OF PAH IN PUF CARTRIDGES IN THE WINTER EXPERIMENT

Compound	Total Amount, μg(a)			Percent of Recovery, %		
	PUF 1R	PUF 2R	PUF 3R	PUF 2R	PUF 3R	Average
D_8-naphthalene	--(b)	0.03	0.03	1.5	1.5	1.5
D_{10}-phenanthrene	--	2.00	1.90	100	95	98
Phenanthrene	4.75	6.50	6.08	88	67	78
Anthracene	0.25	1.72	1.81	74	78	76
Fluoranthene	0.94	2.85	2.64	96	85	91
D_{10}-pyrene	--	1.86	1.77	93	89	91
Pyrene	0.58	2.55	2.40	99	91	95
Cyclopenta[c,d]pyrene	--	0.44	0.47	22	24	23
Benz[a]anthracene	--	1.50	1.42	75	71	73
D_{12}-chrysene	--	1.73	1.63	87	82	85
Benzo[e]pyrene	--	1.83	1.67	92	84	88
D_{12}-benzo[a]pyrene	--	1.22	1.22	61	61	61
Benzo[a]pyrene	--	1.35	1.35	68	68	68

(a) PUF 1R was the non-spiked sample; PUF 2R and PUF 3R were spiked with 2 μg of the listed PAH prior to sampling; a total of 273 m^3 of air was sampled.

(b) Not detected.

TABLE 5.3. LEVELS AND RECOVERIES OF PAH IN XAD-2 CARTRIDGES IN THE SUMMER EXPERIMENT

Compound	Total Amount, μg(a)			Percent of Recovery, %		
	XAD 1	XAD 2	XAD 3	XAD 2	XAD 3	Average
D_8-naphthalene	--(b)	1.35	1.71	68	86	77
D_{10}-phenanthrene	--	1.73	2.02	87	100	94
Phenanthrene	41.5	40.1	37.2	-70.0(c)	-220(c)	-140(c)
Anthracene	0.81	2.18	2.77	69	98	84
Fluoranthene	9.98	11.3	12.8	66(c)	140(c)	100
D_{10}-pyrene	--	1.68	1.85	84	93	88
Pyrene	2.88	4.28	5.53	70	130	100
Cyclopenta[c,d]pyrene	--	2.22	2.31	110	120	120
Benz[a]anthracene	--	1.26	1.37	63	69	66
D_{12}-chrysene	--	1.57	1.87	79	94	87
Benzo[e]pyrene	--	1.34	1.54	67	77	72
D_{12}-benzo[a]pyrene	--	0.97	0.96	49	48	49
Benzo[a]pyrene	--	0.99	1.11	50	56	53

(a) XAD 1 was the non-spiked sample; XAD 2 and XAD 3 were spiked with 2 μg of the listed PAH prior to sampling; a total of 273 m^3 of air was sampled.

(b) Not detected.

(c) The recovery cannot be accurately addressed due to high background levels.

TABLE 5.4. LEVELS AND RECOVERIES OF PAH IN XAD-2 CARTRIDGES IN THE WINTER EXPERIMENT

Compound	Total Amount, μg[a]			Percent of Recovery, %		
	XAD 1R	XAD 2R	XAD 3R	XAD 2R	XAD 3R	Average
D_8-naphthalene	--[b]	1.74	1.87	87	94	91
D_{10}-phenanthrene	--	1.82	1.76	91	88	90
Phenanthrene	4.71	6.35	5.89	82	59	71
Anthracene	0.21	1.64	1.74	72	77	75
Fluoranthene	0.72	2.50	2.76	89	100	95
D_{10}-pyrene	--	1.89	1.80	95	90	93
Pyrene	0.47	2.27	2.42	90	98	94
Cyclopenta[c,d]pyrene	--	1.13	1.18	57	59	58
Benz[a]anthracene	--	1.55	1.60	78	80	79
D_{12}-chrysene	--	1.91	1.65	96	83	90
Benzo[e]pyrene	--	1.80	1.56	90	78	84
D_{12}-benzo[a]pyrene	--	1.24	1.26	62	63	63
Benzo[a]pyrene	--	1.49	1.55	75	78	77

(a) XAD 1R was the non-spiked sample; XAD 2R and XAD 3R were spiked with 2 μg of the listed PAH prior to sampling; a total of 273 m^3 of air was sampled.

(b) Not detected.

TABLE 5.5. LEVELS OF PAH FOUND IN THE FIELD PUF AND XAD-2 RESIN BLANK SAMPLES

Compound	Total Amount, μg[a]			
	PUF B1	PUF B2	XAD B1	XAD B2
D_8-naphthalene	--[b]	--	--	--
D_{10}-phenanthrene	--	--	--	--
Phenanthrene	0.31	0.17	0.17	0.12
Anthracene	0.08	0.01	0.04	0.01
Fluoranthene	0.10	0.05	0.04	0.05
D_{10}-pyrene	--	--	--	--
Pyrene	0.09	0.02	0.07	0.02
Cyclopenta[c,d]pyrene	--	--	--	--
Benz[a]anthracene	--	--	--	--
D_{12}-chrysene	--	--	--	--
Benzo[e]pyrene	--	--	--	--
D_{12}-benzo[e]pyrene	--	--	--	--
Benzo[a]pyrene	--	--	--	--

(a) PUF B1 and XAD B1 are the field blanks from the summer experiment; PUF B2 and XAD B2 are the field blanks from the winter experiment; total amount denotes the amount of PAH found in one PUF or XAD-2 resin cartridge.

(b) Not detected.

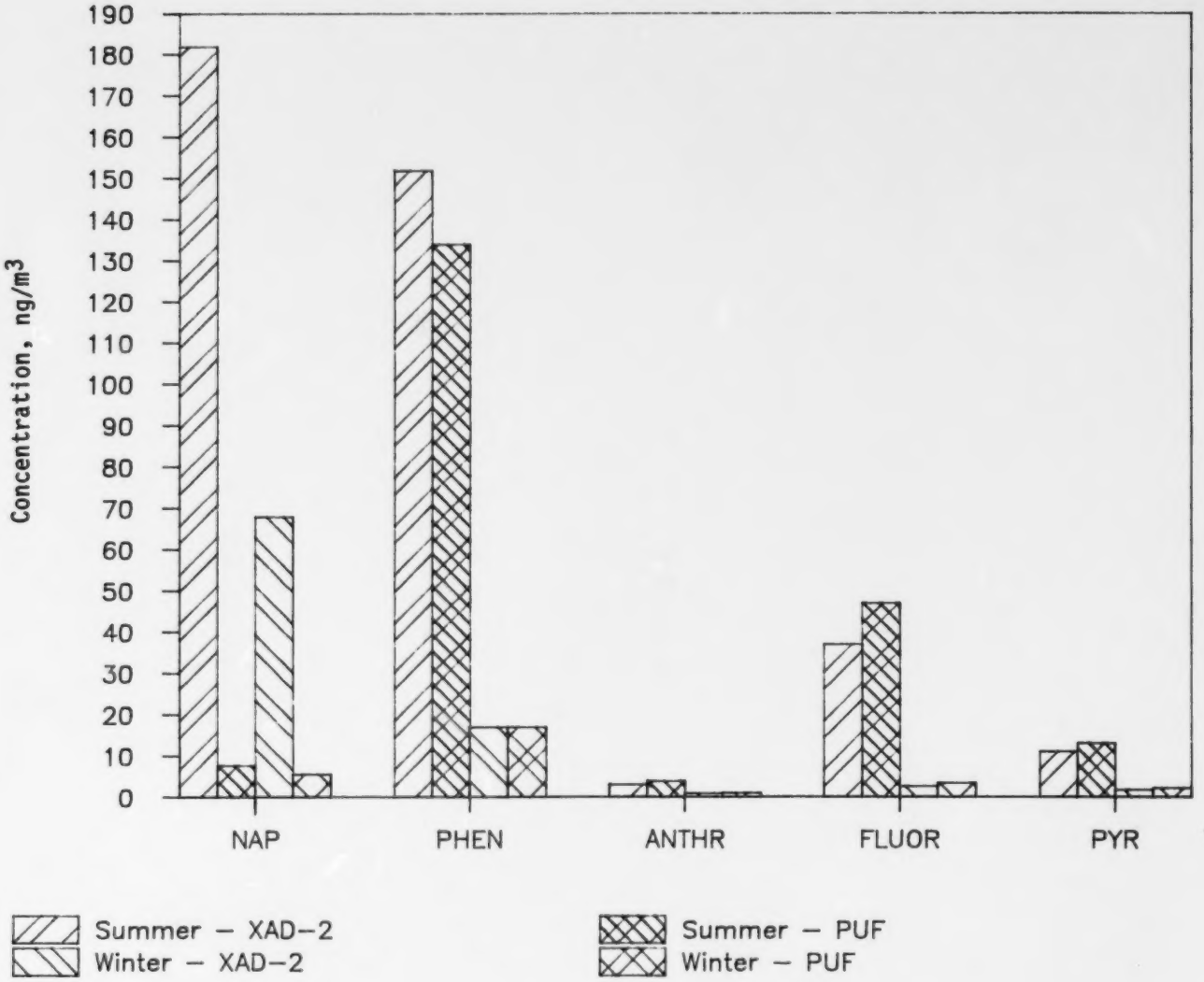

FIGURE 5.1 LEVELS OF NATIVE PAH ADSORBED ON THE NON-SPIKED PUF AND XAD-2 CARTRIDGES IN THE SUMMER AND WINTER EXPERIMENTS

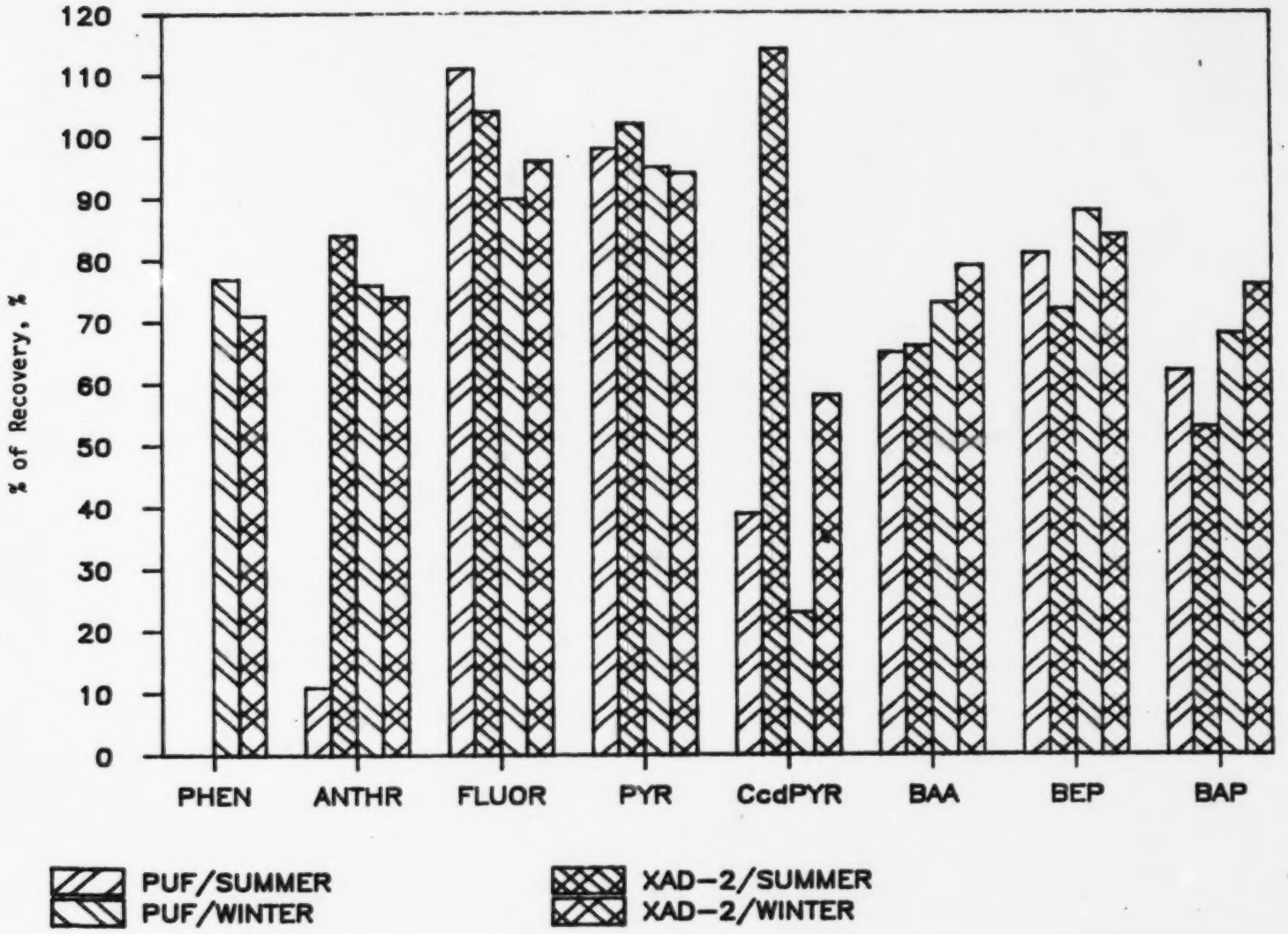

FIGURE 5.2 RECOVERIES OF SPIKED NATIVE PAH IN PUF AND XAD-2 CARTRIDGES IN THE SUMMER AND WINTER EXPERIMENTS

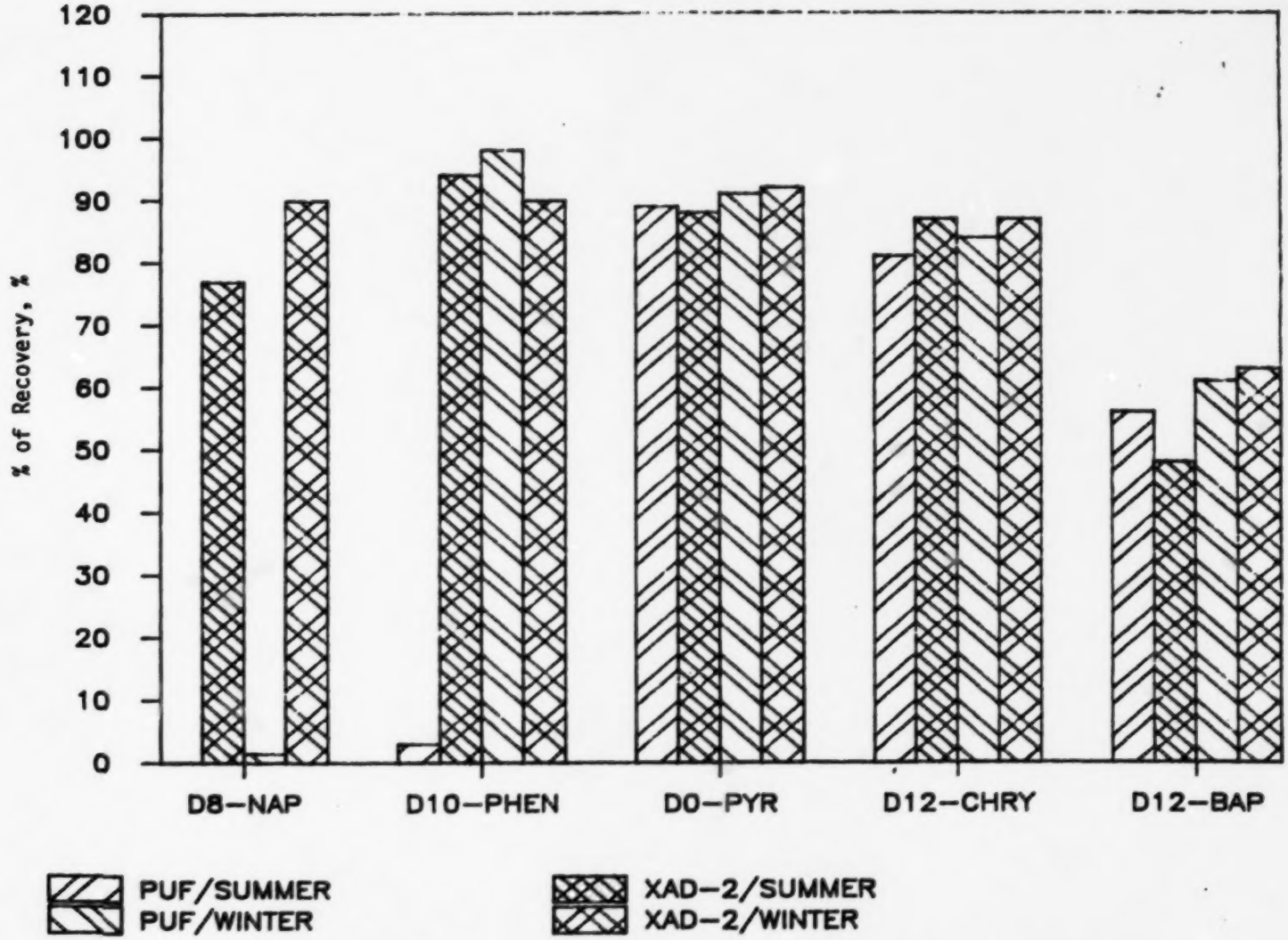

FIGURE 5.3 RECOVERIES OF SPIKED PERDEUTERATED PAH IN PUF AND XAD-2 CARTRIDGES IN THE SUMMER AND WINTER EXPERIMENTS

winter experiments. The levels of phenanthrene were slightly higher in the XAD-2 resin cartridge than in the PUF cartridge from the summer experiment, but the phenanthrene levels in the PUF cartridge were identical to those in the XAD-2 resin cartridge from the winter experiment. These results show that XAD-2 resin has better collection efficiency for volatile PAH than does PUF. In addition, the collection efficiency of PUF for a 3-ring PAH, phenanthrene, can be improved and is comparable to the collection efficiency of XAD-2 resin at the lower sampling temperatures. The differences in lvels of the remaining PAH collected on PUF and XAD-2 resin were less than 10 percent, with no significant trend toward higher or lower levels with either adsorbent. In general, only 2- to 4-ring PAH were collected on the background adsorbents, and the 5- to 7-ring PAH were predominantly retained on the front filters as expected. Higher naturally-occurring PAH ambient air levels were found in the summer experiment than in the winter experiment.

The spiked PAH recoveries from the PUF and XAD-2 resin cartridges were determined by subtracting the levels of PAH in a non-spiked sample from those in the corresponding spiked sample, and dividing by the spiked level (2 µg). In general, good recoveries were obtained for most spiked PAH from both adsorbents after exposure to ambient air at 6.7 cfm for 24 hours at both summer and winter ambient temperatures. The spiked XAD-2 resin gave substantially higher D_8-naphthalene recoveries, however, than did the spiked PUF. An average of 76.5 percent of D_8-naphthalene was recovered from XAD-2 resin even at the summer sampling temperatures (66-86°F), and 90.3 percent recovery for D_8-naphthalene was obtained in the winter experiment (17-27° F). The recoveries of D_8-naphthalene from the PUF cartridges were less than 5 percent in both the summer and winter experiments. Thus, the XAD-2 resin was far more effective in retaining this volatile 2-ring PAH.

Lower recoveries of spiked D_{10}-phenanthrene and spiked native anthracene were observed from the PUF than from the XAD-2 resin at the summer sampling temperatures. These recoveries from the PUF cartridges improved significantly at the winter sampling temperatures, however, and were comparable to the recoveries obtained from the XAD-2 resin cartridges. It should be noted that there was no significant difference between the anthracene naturally-occurring

levels determined from the PUF and the XAD-2 resin cartridges. Since anthracene was not spiked onto the adsorbent in a manner similar to natural PAH vapors, the breakthrough problem with this study may be more severe than in the real world situation. However, the volumetric and gravimetric capacities should be independent at these low concentrations. Nevertheless, temperature is one of the most important factors to be considered in ambient air sampling.

The phenanthrene recovery data cannot be accurately addressed in the summer experiment, because the average ambient air background level was 39.1 µg, which is considerably higher than the spiked level (2 µg). Due to the variation in the sampling and analytical procedures, negative recoveries were obtained in some cases. For the same reason, the recoveries of fluoranthene cannot be accurately addressed in the summer experiment. In the winter experiment, the phenanthrene ambient background levels decreased to 4.7 µg and good recoveries were obtained for both adsorbents.

Lower recoveries of cyclopenta[c,d]pyrene were observed from the PUF cartridges than from the XAD-2 resin cartridges; however, these recoveries did not improve at the lower sampling temperatures. In fact, the recoveries of this compound from both adsorbents were smaller at the lower sampling temperatures. We believe that the losses of cyclopenta[c,d]pyrene are not through volatilization, but are mainly due to the oxidative instability of this compound. The recovery data for the remaining PAH were good, and better retention of some PAH was observed at lower sampling temperatures for both adsorbents. It appeared that XAD-2 resin has higher collection or retention efficiency for volatile and reactive PAH, and that the collection and retention efficiency for some volatile PAH can be improved by lowering the sampling temperature.

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